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# EVALUATION OF SOLIDIFICATION/STABILIZATION FOR TREATING HAZARDOUS WASTE IN THE UNITED STATES

by

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# EVALUATION OF SOLIDIFICATION/STABILIZATION FOR TREATING HAZARDOUS WASTE IN THE UNITED STATES

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ABSTRACT
In hazardous waste management, solidification/stabilization (S/S) is a term normally used to designate technology employing additives to alter hazardous waste to reduce the mobility of pollutants, thereby making it acceptable for land disposal or other uses. The use of this technology to treat hazardous waste in the United States may become more important as regulations restrict the use of land for disposing of untreated hazardous waste. This paper discusses the technology and a program evaluating its potential for managing hazardous waste and contaminated soils in the United States. This paper also presents the United States Environmental Protection Agency (USEPA) research program, and discusses research needed to better utilize S/S as technology to treat hazardous waste.

## INTRODUCTION

In the United States, disposal to the land has been the major technology used to manage waste materials. Favorable economics, previous regulations, and convenience enhanced the use of land disposal. The Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments (HSWA) have, however, provided incentives and controls to encourage treatment of hazardous waste and to reduce the use of land for managing hazardous waste. These regulations require minimum technology standards for designing and operating the hazardous waste land disposal facilities. Regulations ban the disposal of free liquids into landfills and are also banning selected wastes from land disposal. These factors are favoring the use of technologies other than land disposal for waste management.

Important aspects of these bans are that alternatives be available for treating the banned waste and that these alternatives be environmentally acceptable. Some alternative treatment techniques will produce residues requiring management as hazardous waste, and additional treatment may be required before land disposal.

As part of the waste banning activities, the United States Environmental Protection Agency (USEPA) is evaluating solidification/stabilization (S/S) for treating banned waste and hazardous residues from other treatment technologies. The S/S technology employs selected materials (e.g., Portland cement, fly ash, lime) to alter the physical and chemical characteristics of the waste so the mobility of land-disposed pollutants will be reduced. As USEPA proceeds to

implement the waste-banning legislation, S/S technology may assume a very important role in treating hazardous waste.

This paper describes the S/S technology and discusses some of the factors important in determining its usefulness as a waste treatment technology and some of the USEPA S/S programs being pursued.

## OBJECTIVES OF S/S TECHNOLOGY

When using S/S to treat a waste, the broad objective is to contain the pollutant in the waste and prevent it from entering the environment. In practice, this broad objective is realized through several mechanisms which are to produce a solid, to decrease the surface area across which the contaminant can be transported, to limit the mobility of the contaminant when exposed to leaching fluids, and to improve handling characteristics of the waste.

Ideally, the objective is to completely transform the potentially toxic contaminant into a nontoxic form. This objective implies chemical transformation and formation of new compounds. Realistically, chemical changes of the contaminant do not routinely occur with the available state-of-the art S/S technologies.

## DESCRIPTION OF S/S TECHNOLOGY

### Definitions

Definitions for S/S technology vary depending upon the source. In very general terms, S/S, as it relates to managing hazardous waste, refers to a technology where one uses additives to transform the waste into a more manageable form or a less toxic form by physically and/or chemically immobilizing the waste constituents. It is important to understand the terminology to properly evaluate the technology for potential application.(1)
The following definitions are used in this paper:

Solidification is a process in which materials are added to a liquid or semi-liquid waste to produce a solid.

Stabilization refers to a process by which a waste is converted to a more chemically stable form.

Chemical Fixation implies the transformation of toxic contaminants to a new nontoxic form.

Encapsulation is a process involving the complete coating or enclosure of a toxic particle or waste agglomerate with a new substance, e.g., the S/S additive or binder. Microencapsulation is the encapsulation of individual particles. Macroencapsulation is the encapsulation of an agglomeration of waste particles or microencapsulated materials.

## Binders

Binder systems can be placed into two broad categories, inorganic or organic. Must inorganic binding systems include varying combinations of hydraulic cements, lime, pozzolans, gypsum, and silicates. Organic binders can include epoxy, polyesters, asphalt/bitumen, polyolefins (primarily polyethylene and polyethylene-polybutadiene), and urea-formaldehyde. Combinations of inorganic and organic binder systems include diatomaceous earth with cement and polystyrene, polyurethane and cement, and polymer gels with silicate and lime cement.(2)

Knowledge of the binders used for waste S/S can be important in assessing and therefore selecting a specific process. It provides insight into processing requirements, waste pretreatment requirements, waste-binder interactions, and expected product performance under different disposal options. The quantity and type of binder can be selected and varied to provide the desired solidified waste characteristics.

## Binding Mechanisms

Several mechanisms act to bind or hold the pollutant and make it less mobile.(3) These include:

Sorption involves adding a solid to take up any free liquid in a waste. Examples are activated carbon, anhydrous sodium silicate, gypsum, clays, and similar particulate materials.

Lime-Fly Ash Pozzolan Reactions employ a fine, noncrystalline silica in fly ash and the calcium in lime to produce low-strength cementation. Physical trapping of the contaminant in the cured pozzolan cooncrete matrix is the primary containment mechanism. Water is removed in hydrating the lime-pozzolan concrete.

Pozzolan Portland Cement Reactions combine Portland cement and fly ash or other pozzolans to produce a relatively high strength waste/concrete matrix. Waste containment is primarily by entrapment of waste particles. Soluble silicates may be added to aid processing and to assist in metal containment through the formation of silicate gels.

Thermoplastic Microencapsulation blends waste particulates with melted asphalt or similar materials. Physical entrapment is the primary containment mechanism.

Macroencapsulation isolates a large volume of waste by jacketing it with any acceptable material. A 55-gal drum is a simple example. More sophisticated and superior performance macroencapsulation processes employing polyethylenes and similar resins in the containment vessel have been investigated.(4,5)

Other S/S technologies have been proposed or investigated but are experimental, expensive, difficult to implement, or not widely used. An example would include vitrification (fusing a waste into a vitreous mass).

Process Types

Several S/S processing schemes available for consideration include:

In-Drum Processing adds the S/S binders to the waste contained in a drum or other container. After mixing and setting, the waste-binder matrix is normally disposed of in the drum.

In-Plant Processing refers to a plant or process both specifically designed for S/S of bulk waste material. This may be a process conducted within a plant to manage the waste from an internal industrial operation or may be a plant specifically designed and operated to solidify/stabilize waste from external sources.

Mobile Plant Processing refers to S/S processes and equipment that are either mobile or can be easily transported and set up from one site to another.

In-situ Processing refers to adding binders directly to a lagoon or injecting S/S materials to the soil subsurface to promote the S/S of the contaminated sludge or soil or both.

The USEPA Program in Solidification/Stabilization

The USEPA is pursuing two main activities in solidificaton/stabilization: evaluating S/S as a best demonstrated available technology for treating hazardous waste and conducting research to develop a more comprehensive scientific understanding of the technology.

Evaluating S/S for Treating Hazardous Waste

A program is being conducted in which selected hazardous wastes are solidified/stabilized by several pozzolanic processes, and the solidified products further tested for chemical and physical characteristics. The S/S processes use Portland Cement, cement kiln dust, and lime/fly ash mixtures as binder materials. Initially, a screening study is conducted to determine the amount of water to be used for each of the binders. Each binder system is then evaluated by preparing batches with different ratios of waste to water to binder mixtures, allowing them to cure for 28 days, and testing the cured material.

A minimum of four binder/waste ratios is evaluated for each binder system. Additionally, each batch is prepared three times in order to assess any variability inherent to the stabiliztion process. The cure rate of each binder/waste ratio is characterized by performance of the Unconfined Strength Test (UCS) after a cure time of 7, 14, 21, and 28 days. After the 28-day cure time, the binder/waste ratio with a UCS nearest to, but at least 50 psi for each binder system is subjected to the USEPA's Toxicity Characteristic Leaching Procedure (TCLP) extraction and percent moisture analysis. The leachate from the TCLP will be analyzed for the pollutants of concern on the United States RCRA list of hazardous wastes (Table 1). These results will be used to determine how effective S/S can be for treating these listed hazardous wastes. Additional wastes will be investigated as the USEPA proceeds with the land banning activities.

In a companion program, mixtures of soils contaminated with selected chemicals are being solidified/stabilized, and the solidified/stabilized products are further tested to develop information on S/S as a technology for cleaning up contaminted soils and debris at Superfund sites (Table 2). The test soil being used is a mixture of clay, sand, silt, topsoil and aggregate.

Screening, testing and analytical procedures similar to those described for the RCRA listed hazardous waste program are being used to evaluate the effectiveness for solidification to treat the contaminated soils.

TABLE 1

U.S. RCRA Hazardous Wastes for Which Solidification/Stabilization is Being Evaluated as a Treatment Technology

| USEPA Waste Code | Description of Waste | Pollutant of Concern |
|---|---|---|
| F006-8 | Wastewater treatment sludges for electroplating operations except from the following processes (1) sulfuric anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc, and aluminum plating on steel; and (6) chemical etching and milling of aluminum | Cadmium, Hexavalent chromium, Nickel, Cyanide (complexed) |
| | Plating sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process | Cyanide (salts) |
| K048-52 | Dissolved air flotation (DAF) float from the petroleum refining industry | Hexavalent chromium, lead |
| | Slop oil emulsion from the petroleum refining industry | Hexavalent chromium, lead |
| | Heat exchanger bundle cleaning sludge from the petroleum refining industry | Hexavalent chromium |
| | API separator sludge from the petroleum refining industry | Hexavalent chromium, lead |
| | Tank bottoms (leaded) from the petroleum refining industry | Lead |
| K061 | Emission control dust/sludge from the primary production of steel in electric furnaces | Hexavalent chromium, lead, cadmium |
| K046 | Wastewater treatment sludges from the manufacturing formulation and loading of lead-based initiating compounds | Lead |

TABLE 1 (cont'd)

U.S. RCRA Hazardous Wastes for Which Solidification/Stabilization is Being Evaluated as a Treatment Technology

| USEPA Waste Code | Description of Waste | Pollutant of Concern |
|---|---|---|
| K086 | Solvent washes and sludges, caustic washes and sludges, or water washes and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead | Lead, hexavalent chromium |
| K004 | Wastewater treatment sludge from the production of zinc yellow pigments | Hexavalent chromium |
| | Oven residue from the production of chrome oxide green pigments | Hexavalent chromium |
| K106 | Wastewater treatment sludge from the mercury cell process in chlorine production | Mercury |
| K031 | By-product salts generated in the production of MSMA (mono sodium methyl arsenate) and cacodylic acid | Arsenic |

TABLE 2

Contaminants Added to Test Soils Being Used to Evaluate Effectiveness of Solidification for Superfund Sites

| Metals | Volatiles | Semi-Volatiles |
|---|---|---|
| Lead | Acetone | Benzo(a) pyrene |
| Zinc | Ethylbenzene 1, 2 Dichloroethane | Pentachlorophenol |
| Cadmium | Xylene | Naphthalene |
| Copper | Tetrachloroethylene | |
| Nickel | Chlorobenzene | |
| Chromium | | |

In conjunction with these S/S evaluation programs, laboratory facilities and procedures are being established to test samples of solidified waste extracted from actual field operations. These facilities will also be able to assist in determining if a particular contaminated soil or waste is capable

of being effectively solidified/stabilized. Because the laboratory is equipped to conduct different leaching and physical tests, (i.e., TCLP, equilibrium batch, sequential, freeze-thaw, wet-dry, permeability, etc.), a full evaluation of the solidified waste can be conducted. Data from this program will assist investigators to extrapolate laboratory test results and help to better predict expected long term field performance.

In addition, the USEPA Superfund Innovative Technology Evaluation (SITE) program is providing an opportunity to evaluate the performance and effectiveness of S/S to clean-up contaminated sites under actual field conditions. The SITE program which provides for the demonstration and evaluation of innovative technologies to remediate superfund sites includes several solidification processes. This will provide another link between laboratory research and field performance of S/S for managing hazardous waste.

## CURRENT USEPA RESEARCH

In the current USEPA program (Table 3), research has emphasized investigating interferences to S/S, investigating waste-binder interaction and waste disposition sites, and study of methods for predicting performance of S/S products.

The research on intefering agents will provide data on the effects that interfering inorganics (Pb, Cd, Zn, sulfates, etc.) and organics (oil, grease, HCB, TCE, phenol) have on generally used pozzolanic binder systems (without proprietary additives). The information will be useful in evaluating applications for delisting hazardous waste and for permits to treat hazardous wastes with S/S, particularly for those waste streams contaminated with organics. This information and that from research on factors critical to S/S will also aid decisions on potential waste pretreatment techniques for enhancing S/S performance.

A cooperative effort with Canada is emphasizing evaluation and comparison of several leaching tests for determining the extent of toxic constituent binding. Protocols for examining physical properties are also being evaluated. Because this research includes actual waste and synthetic sludges solidified by vendors, information on the performance of several different solidified products can be compared. This research will also provide important data to compare current regulatory leaching procedures with others being tested in the program.

Various microscopy techniques and solvent extractions are being used to investigate waste/binder interactions. The prime objective is to gain a better scientific understanding of S/S by understanding binder reaction phases

TABLE 3

Current USEPA Solidification/Stabilization Research Projects

| Project Title | Objective | Status |
|---|---|---|
| Evaluation of Factors Affecting Solidification/ Stabilization of Toxic Waste | Determine effects of interfering agents on performance of S/S | Three binders (cement, cement-fly ash, and lime fly ash have been prepared; physical tests completed; chemical tests proceeding; one binder remaining |
| Investigation of Test Methods for Solidified Waste Characterization - A Cooperative Program | Develop and evaluate methods for testing performance of solidification processes. 13 commercial vendors, Environment Canada and USEPA are cooperating in this study | All testing should be completed by October 1987 |
| Study of Morphology and Microchemistry of Solidified/ Stabilized Waste | Determine waste deposition sites in waste-binder matrix and investigate bonding mechanisms by use of microscopy techniques | Research is continuing |
| Morphological Examination of S/S Samples from Canadian-US Study | Provide morphological examination of solidified waste specimens from Canada-US study; correlate morphology and waste disposition with physical/ chemical test of actual samples | Ongoing |
| Critical Characteristics and Properties of Hazardous Waste Solidification/ Stabilization | Identify physical and chemical characteristics of waste and binders affecting S/S; provide information or potential waste pretreatment techniques | Completed |
| Air Emissions From Waste Stabilization | Provide USEPA information on potential air emissions from S/S processes | Ongoing |

TABLE 3 (cont'd)

Current USEPA Solidification/Stabilization Research Projects

| Project Title | Objective | Status |
|---|---|---|
| Evaluation of S/S for Treating Ash Residues | Provide data on use of S/S for treating residues from the combustion of municipal solid waste | Ongoing |

where the waste components concentrate their form, and the waste is bonded. Concurrent with this research, specimens of solidified waste from the other research projects are being examined in efforts to better understand and correlate results of physical and chemical tests with performance of S/S products.

There are factors that are extremely important and which will affect the performance of S/S. The physical and chemical characteristics of the waste are important to performance but also are the climatic (temperature and humidity) conditions at the time of placement and curing of the S/S product. The research on critical characteristics of hazardous waste S/S will be expanded to developed information on what type of quality assurance control procedures will be required to better assure adequate performance of S/S when applied in the field.

Fly ashes and bottom ashes from the combustion of municipal waste combustion may contain unacceptable levels of heavy metals, particularly lead and cadmium. Solidification/stabilization technology is being evaluated as an acceptable technique to control these ashes if required. The USEPA and Canada are conductng research in this area.

## The Future of Solidificaton/Stabilization in the United States

Whether or not S/S becomes an important technology for treating hazardous waste in the United States ultimately depends upon regulatory requirements and the capability of the technology to meet these requirements. As performance criteria become more severe, vendors may need to improve their processes.

Factors important in the selection, design, implementation, and performance of S/S processes and products are as follows: waste characteristics (chemical and physical), process type and processing requirements, S/S product management objective, regulatory requirements, and economics. These and other site-specific factors (i.e., location, condition, climate, hydrology, etc.) must be carefully considered to ensure acceptable performance.

The chemical effects of some compounds can reduce the strength and containment characteristics of the binder/waste mix, while some compounds can accelerate or retard the S/S product. Temperature and humidity can retard or accelerate the setting. The physical characteristics of size and shape of waste can affect the viscosity of the mix, and overmixing or undermixing can affect the product's strength. The characteristics of the wastes are among the most important factors affecting waste S/S. Inorganics usually can be more easily solidified/ stabilized than can organics.

It is important that the correct process type and specific process requirements required are assessed to evaluate and select an S/S technology. For example, a waste-binder can be controlled and mixed more easily in a drum or in a plant process than in the in-situ solidification of a pit, pond, or lagoon.

The management objective sought is another important factor. Is the binder-waste to be disposed of in a landfill, or stored, or transported? Will it be placed in a plastic or metal drum? Stored in a warehouse or underground mine? Assessing objectives such as these are important in selecting the best-suited S/S technique or system.

The regulatory factors in the United States will be a critical factor. Except for possibly four tests or procedures (Paint Filter Liquids Test, PFLT; Extraction Procedure, EP; Modified Extraction Procedure, MEP; and Toxicity Characteristics Leaching Procedure, TCLP), there are no performance criteria that S/S products must now meet. Theoretically, almost any waste can be solidified, or stabilized, or both, and systems and processes can be altered to meet different performance criteria, and these criteria will become increasingly stringent. Before selecting a particular S/S technique, determine the regulatory criteria.

Costs of the S/S process must be considered. Final costs will depend on site-specific conditions. The important factors are the waste's characteristics, transportation, type of process, and some special factors. What is the physical form and chemical make-up of the waste? Is pretreatment needed? Are raw materials transported to the plant or site? Are finished S/S products shipped to final disposal? Which S/S process and which process type (e.g., in-drum) is needed. What special health and safety requirements are needed? Is a quality assurance/quality control cost involved? What regulatory factors must be met? Each and all of these factors need to be considered to determine the cost for each waste to be disposed of.

Needs for S/S as a Treatment Technology

For S/S technology to be effective in managing hazardous waste, proposed processes must be properly selected, formulated, and used. Several factors important in the performance of candidate processes include the waste's physical and chemical characteristics, interactions of binder/waste and impurities in the matrix, and product placement regime. Improved knowledge of these factors and the interactions that can be expected among the various candidate binders and waste types is critical to the successful use and evaluation of S/S for managing hazardous waste and, therefore, its role as an acceptable treatment technology for hazardous waste.

Studies are needed:

- to determine the long-term physical-chemical stability of S/S residues when placed on the land;
- to determine how and under what conditions S/S residues should be placed on the land to ensure environmental protections over the long term;
- to predict and measure the performance of S/S processes and products;
- to provide a correlation between regulatory criteria and real-world situations;
- to evaluate the effectiveness of several protocols (e.g., TCLP, other leaching tests, unconfined compressive strengths, etc.) that will characterize S/S products, provide effective measurement techniques, and correlate results of such tests with prediction of performance in the field;
- to determine or evaluate the effectiveness of processes and equipment that will effectively solidify/stabilize the contaminated soil and/or lagoon and the effectiveness of mixing methods and the resulting solidified/stabilized soil performance at varying soil depths;
- to determine the amounts of organic compounds that can be included in inorganic waste streams without requiring pretreatment before S/S or that will not adversely affect the S/S product performance;
- to determine how effectively S/S processes treat residuals from other alternative treatments so that the long-term performance of S/S products can be predicted.

Such information is needed to develop adequate technology performance standards for S/S to treat selected wastes.

## Summary and Conclusions

This paper describes S/S as a technology using binders (additives) to manage hazardous wastes. It is a relatively simple and inexpensive technology that has been used for over 20 years in the United States to treat industrial waste. The USEPA is evaluating S/S as a treatment technology which will make wastes acceptable for land disposal. If it is an acceptable alternative treatment, the technology will play an increasingly important role in managing hazardous wastes banned from land disposal and hazardous residues from other alternative treatments.

Important factors affecting the selection and use of S/S include: the waste's chemical and physical characteristics, process type requirements, product management objective, regulatory requirements and economics. Whether or not S/S is an effective alternative technology greatly depends on the changing regulatory criteria that S/S will have to meet and on whether vendors can use existing processes or develop new ones to meet potentially more demanding performance requirements.

A better scientific understanding of S/S processes is needed for further development of S/S as an alternative treatment. The overview given of current USEPA research indicates the support for these research needs.

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